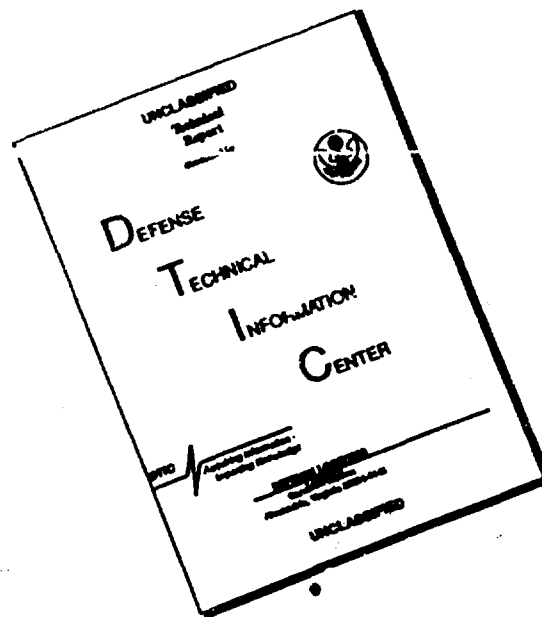


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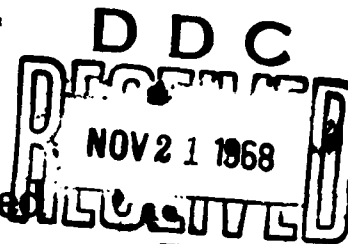


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Original Articles

A New Hazard in Closed Environmental Atmospheres

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THE CONVERSION of trichloroethylene to dichloroacetylene, an exceedingly toxic material, is well known to anesthesiologists.¹ The circumstances found by anesthesiologists necessary for formation of dichloroacetylene have been brought together again coincidentally in many of the life support systems necessary to the extended closed cycle habitation of nuclear submarines and extraterrestrial spacecraft. One serious incident in which a crew was incapacitated by the production of dichloroacetylene in a closed environmental atmosphere has already been reported.^{2,3} The following is an account of that incident and its solution.

Recently, the National Aeronautics and Space Administration sponsored a Manned Environmental Systems Assessment, project MESA. The MESA experiments, conducted by the Boeing Company in 1963, were the first to evaluate a completely integrated and regenerative air, water, and biological life support system. The purpose of the tests was to determine the effectiveness of one such system for extraterrestrial space travel by maintaining five men in a completely closed environment for 30 days.

Many secondary experiments were scheduled for inclusion in this project. These required considerable extra equipment in the

chamber in addition to the life support system. The chamber also contained all food and other supplies required to maintain the five-man crew for 30 days. Much of these materials were organic and were recognized as potential sources of atmospheric contaminants.

The essential elements of the air contaminant control section of the life support system were charcoal and silica gel adsorbent beds, lithium hydroxide and sodium superoxide filter units, and a catalytic oxidizer containing copper and manganese oxides. The sodium superoxide unit served the triple function of carbon dioxide removal, adsorption of acid gases, and the regeneration of oxygen. The purpose of the catalytic oxidizer was to convert carbon monoxide and hydrogen to carbon dioxide and water, respectively, and additionally to perform as an efficient hydrocarbon incinerator.

A preliminary two-day unmanned test of the entire system was completed without difficulty before the start of the manned test. Like many complicated experiments, however, the first attempt at the main event was plagued with difficulties. To name a few: electrical insulation on a pair of heater leads charred and evolved a disagreeable odor; neoprene ducting carrying heated gases between units of the air purification system also emitted an unpleasant odor; several mechanical difficulties were encountered with the biological waste reactor which required the unpleasant task of periodic cleaning of the unit in situ. None of these events had any effect on the situation as it later developed except to add to the complexity of the problem.

Parts of the sodium superoxide unit were fabricated from aluminum. The action of

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atmospheric moisture on the superoxide resulted in a solution of sodium hydroxide which wetted some of the aluminum parts and resulted in the production of hydrogen. The steady evolution of hydrogen into the atmosphere necessitated passing the chamber air through the catalyst burner at a rate faster than originally planned. This increased flow rate through the catalytic oxidizer exceeded its design rate and dropped the temperature of the catalyst bed considerably below its optimum operating temperature. Studies of the catalyzed combustion of organic atmospheric contaminants made at the Naval Research Laboratory with the same catalyst mixture have shown a not surprising decrease in combustion for less-than-optimum catalyst temperatures.⁴ Some contaminants are completely decomposed to carbon dioxide and water, but with low efficiency, while others, such as certain chlorinated hydrocarbons, are only partially decomposed, with the formation of intermediate decomposition products.

As a result of the lowered efficiency of the catalytic oxidizer in the MESA chamber, the atmospheric contaminant load increased fairly rapidly. In less than 48 hours, the atmosphere acquired a very distinct, sickening, sour-sweet odor which became increasingly irritating to the crew. The crew soon lost their appetites and their general feeling of well-being began to deteriorate.

After the third and fourth day of exposure to the chamber atmosphere, the crew's nausea progressed to vomiting; the men developed itching around the eyes, headaches, sore gums, and painful jaws. To further compound their discomfort, the glass in the sight gauge of the sewage processing plant burst and raw sewage spilled across the chamber floor. The crew (already feeling considerably subpar) at this point elected to abort the test in the middle of the fourth day.

All the symptoms experienced by the MESA crew were thought by the medical personnel in attendance to be caused by atmospheric contamination. Oddly, the crew developed rather severe cold sores shortly after the premature abortion of the test. These cold sores were also attributed by test personnel to chemical irritation by the

chamber atmosphere and not to viral infection. Two other symptoms, the itchy eyes and the pains in the gums and jaws, were also rather unusual. Most of the symptoms persisted for several days before finally subsiding.

There was a great deal of interest in the identity and source of the causative agent. Many samples were taken from various points in the chamber and sent to several laboratories for analysis. A 60-gm sample of adsorbent charcoal, received at the Naval Research Laboratory, had been exposed in the chamber for 48 hours following the aborted completion of the experiment, but during a time when the odor in the chamber was still strong. The desorbant mixture from that charcoal was resolved into its individual components by a vapor phase chromatograph. Each separated component was collected individually from the effluent stream and subsequently specifically identified by its infrared or mass spectrum.

The various contaminants recovered from the charcoal are as follows.

Contaminants Identified in MESA Atmosphere

Trichloroethylene	Ethyl Chloride
Dichloroacetylene	Carbon Disulfide
Monochloroacetylene	Vinylidene Chloride
Carbon Dioxide	Dichlorodifluoromethane
N-Pentane	(Freon-12)
Ethanol	Ammonia
Acetaldehyde	Methyl Chloride
Carbonyl Sulfide	Ethyl Ether
Propylene	2 Methyl Butene
N-Butane	Acetone
Isobutylene	Methanol
Isopentane	Methyl Ethyl Ketone

Except for two, these compounds are common and have been found many times before in other environmental atmospheres. The most prevalent trace contaminant in the MESA atmosphere was trichloroethylene. It was later recalled by project personnel that this solvent had been used in the chamber for cleaning purposes before the start of the manned test. The two uncommon compounds found were monochloroacetylene and dichloroacetylene. Neither of these compounds had ever been found before in a closed atmosphere.

Since both these compounds were known from the chemical literature to be extremely unstable in air,^{5,6} their presence in the

MESA atmosphere was first reported as questionable. The possibility existed that these compounds might have resulted from the thermal decomposition of other chlorinated hydrocarbons during the analytical procedures. Furthermore, no information concerning the toxicity of either of these compounds could be found in the literature usually available to scientists and engineers. Consequently, monochloroacetylene and dichloroacetylene was not seriously considered as a probable reason for the MESA symptoms. No further information developed concerning the MESA atmosphere and the problem of pinpointing the cause of the trouble went unsolved until recently.

A few months ago, dichloroacetylene was detected at very low concentration in one of our nuclear submarine atmospheres. In this instance, the compound was found in a sample of compressed air and was determined to be real and not an analytical artifact. The stability of the compound in air at low concentrations was thus apparent.

Dichloroacetylene can be synthesized by passing trichloroethylene over any of several alkaline materials at a temperature above 70 C. When the compound was synthesized, it did indeed decompose explosively in air at high concentrations, yielding carbon monoxide and phosgene, but was stable at low concentrations. High concentrations decomposing in air left a low residual concentration. The concentration at which the compound is stable depends upon purity. Some compounds such as trichloroethylene will inhibit this decomposition reaction.¹ Concentrations of dichloroacetylene in air up to 200 ppm have been found stable in the presence of such compounds.

The toxicity of dichloroacetylene is well documented in the medical literature. British physicians in the 1940's reported a number of fatalities attributed to dichloroacetylene inhalation poisoning.²⁻⁶ The compound was encountered by patients being anesthetized with trichloroethylene when the anesthetic mixture was administered in a closed system with a machine which incorporated a soda-lime carbon dioxide adsorber. The soda-lime became hot enough to convert trichloroethylene to dichloroac-

etylene as a result of reaction with the moisture and carbon dioxide in the patient's exhaled breath. Anesthetic mixtures of trichloroethylene in air or oxygen (usually 1% by volume) were reported to have given rise to lethal concentrations of dichloroacetylene when administered in this fashion. Fatalities were reported which followed exposures as short as 45 minutes. Unfortunately, the concentrations of toxic material which were inspired by these patients was not determined. Many of those affected, however, had not been given trichloroethylene themselves, but were anesthetized in the closed cycle manner with a machine containing residual trichloroethylene from a previous use.

The symptoms of dichloroacetylene poisoning are unusual and unique. Comparison of the symptoms induced by dichloroacetylene and those exhibited by the MESA crew are as follows.

Mesa Symptoms	Effects of Dichloroacetylene
Loss of appetite	Loss of appetite
Extreme nausea	Extreme nausea
Vomiting	Vomiting
Itchiness around the eyes	Symptoms involving facial muscles
Soreness of gums	
Intense pain in the upper jaw	Headaches
Headaches	
Welts on mouth and lips	
	Facial herpes

Note that the correspondence between the two sets of symptoms is exact. Dichloroacetylene has a pronounced effect upon the trigeminal nerve and, with sufficient exposure, gives rise to circumoral herpetiform lesions. The symptoms develop with increasing exposure in the order listed. The long-lasting effect of the symptoms exhibited by the MESA crew was also noted by the British as characteristic of dichloroacetylene poisoning. Incidentally, the dichloroacetylene prepared at NRL had a disagreeable sour-sweet odor, an odor also noted by the British and one which was particularly annoying in the MESA chamber.

Dichloroacetylene was one contaminant in the MESA atmosphere which accounts for all the rather unusual symptoms exhibited by the crew. No information is avail-

able about the related compound, monochloroacetylene, which was also found in the MESA atmosphere. Possibly, it may induce similar effects.

The presence of dichloroacetylene in the MESA atmosphere is attributable to the partial decomposition of its precursor, trichloroethylene, by the sodium superoxide unit and perhaps, to a lesser extent, by the lithium hydroxide unit. Monochloroacetylene was similarly formed from vinylidene chloride, which was also present in the MESA atmosphere.

The reactions leading to the presence of the dichloroacetylene found in the submarine atmosphere are more involved. Methyl chloroform is a common contaminant in all our nuclear submarine atmospheres because it is used in an adhesive for cementing thermal insulation to pipes and bulkheads. Normally, this contaminant is degraded to carbon dioxide and hydrochloric acid in a properly operating submarine catalytic burner. A lithium carbonate filter is placed downstream from the burner to adsorb the hydrochloric acid and prevent damage from corrosion. On the occasion in question the catalyst unit was operated at less than optimum temperature. Under these conditions, methyl chloroform is not decomposed all the way to carbon dioxide and hydrochloric acid. Two of the partial decomposition products are vinylidene chloride and trichloroethylene.¹⁰ The latter compound is subsequently converted in good yield to dichloroacetylene by the lithium carbonate bed.

Following the aborted MESA test, a second experiment was scheduled which incorporated a modified sodium superoxide unit and an additional large activated charcoal filter. The second experiment lasted 30 days and was completed successfully without difficulty. Since the first MESA experiment, other incidents of suspected dichloroacetylene formation have occurred, one of the most interesting being a French experiment with a high-pressure diving atmosphere (J. Chouteau, oral communication, March 29, 1966). While no atmospheric samples were available in this case to confirm the presence of dichloroacetylene, circumstances were such that its presence was almost certain.

The MESA experiments presented the first serious case of organic trace contamination in a confined environmental atmosphere, serious enough, in fact, to incapacitate a crew, and ironically, the causative agent was not a gas-off product from any cabin material, as might have been expected, but a contaminant actually generated by the contaminant control system.

Many contaminant control systems for closed environmental atmospheres feature catalyst units followed by alkaline acid-adsorbing units. In view of the fact that most such atmospheres typically become contaminated with chlorinated hydrocarbons, a dangerous situation is possible if the catalyst unit fails or its temperature falls to some less-than-optimum level. Some idea of the danger that dichloroacetylene can present in a closed atmosphere is conveyed by the fact that British patients who survived dichloroacetylene exposures barely avoiding permanent damage exhibited only slightly more severe symptoms than those experienced by the MESA crew.

The danger posed to industrial users of technical grade inhibited vinylidene chloride and trichloroethylene by the possible conversion of these solvents to monochloroacetylene and dichloroacetylene appears to be limited to circumstances in which the solvents or their vapors contacted alkaline materials, especially at elevated temperatures. Monochloroacetylene and dichloroacetylene can also be formed in trace quantities from other chlorinated hydrocarbons as a result of pyrolysis and photolysis, however. Certain safety respiratory face mask canisters contain alkaline material and, obviously, these should not be worn in the presence of vinylidene chloride and trichloroethylene vapors. Uninhibited, medical grade trichloroethylene can undergo considerable decomposition from photolysis.¹¹ A one-month exposure to sunlight can generate enough dichloroacetylene to affect seriously the trigeminal nerves of one inhaling fumes from the container.

Summary

A government contractor recently evaluated a completely integrated life support system in an experiment which involved

maintaining five men for 30 days in a hermetically sealed environmental chamber. Undesirable contaminants developed in the chamber and persisted in spite of the contaminant control system. The atmosphere acquired an odor which became increasingly disagreeable. The crew developed anorexia, became nauseated, suffered severe vomiting, and developed headaches and odd facial sensations. These symptoms together with other difficulties prompted test termination after four days. Preliminary efforts to pinpoint the cause of the sickness were unsuccessful.

Later analysis of the chamber atmosphere at the Naval Research Laboratory iden-

tified 23 volatile compounds. Among these were monochloroacetylene and dichloroacetylene. The latter compound is known to produce symptoms identical to those experienced by the chamber crew. Dichloroacetylene has since been found at low concentration in a submarine atmosphere also.

A few chlorinated hydrocarbons customarily have been tolerated in most closed environmental atmospheres because of their general usefulness and relatively low toxicity. Such was the case in both these instances. The toxicant was produced through the action of an improperly operating element of the environmental control system on one of these compounds.

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CHANGES IN MEDICAL-CARE SUPPORT

It is remarkable that even in medical circles the debate over medicare and other major changes in medical-care support has raged almost entirely around the issue of the source and mechanism of payment. Shall it be individual or group prepayment, Social Security or general tax revenue? Excitement about such problems has tended to obscure the more important medical aspect, namely that the real effect on the nature, amount, and quality of care comes not from the source of payment but from the specification of services to be provided. A familiar example is the encouragement of hospitalization for diagnostic services which could be provided just as well or better out of the hospital, when the prepayment benefit is limited to inpatient hospital care. The source of payment does not matter in this instance; it could be either private or governmental, Social Security, or general tax revenue. The determining influence is the specification of the benefit, that is, inpatient hospital care only.—Breslow, L.: Changing Patterns of Medical Care and Support, *J Med Educ* 41:318-324 (April) 1966.

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